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(19) (CA) **CANADIAN PATENT** (12)

(54) Bactericidal and Fungicidal Agent and Aqueous  
Formulations Containing Same

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**Canada**

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The invention is concerned with agents that can be diluted with water, have a bactericidal and fungicidal action and are suitable, especially in aqueous formulations, for example, as wood preservatives, disinfectants, as biocides for paint systems, and for the bactericidal and fungicidal treatment of textiles, plastics materials, adhesives, building materials, paper, leather, drilling and cutting oils and circulating cooling water.

The present invention provides a bactericidal or fungicidal agent comprising: (a) a trialkyltin compound having in the alkyl groups bonded to the tin atom a total number of from 9 to 12 carbon atoms, or a triphenyl-tin compound, excluding triorgan-tin halides, (b) an alkali metal salt of N'-hydroxy-n-cyclohexyldiazenium oxide. The components (a) and (b) are preferably present in a ratio of from 5:1 to 1:5 by weight, especially from 3:1 to 1:3, by weight, respectively.

The agents of the invention are especially suitable for use in aqueous formulations together with customary emulsifiers, and find application, more especially, for protecting wood. In the aqueous formulations the concentration of active ingredient is preferably between 0.05 and 5% by weight, and for protecting wood the concentration is preferably within the range of from 0.1 to 3% by weight.



The invention accordingly also provides an aqueous formulation which contains a bactericidal or fungicidal agent as defined above and water.

The high activity of triorganotin compounds against microorganisms, for example harmful fungi and bacteria, is known. This class of compounds generally has its optimum action when the total number of carbon atoms in the alkyl groups bonded to the tin atom is from 9 to 12. Shorter or longer alkyl groups reduce the biocidal activity. Although triorganotin compounds have a relatively broad range of action against different microorganisms, for example gram-negative bacteria and certain blue fungi, their action is, however, comparatively weak.

DE-PS 1 024 743 describes another group of biocides which is used, for the most part, as wood preservative. These are salts of N'-hydroxy-N-alkyldiazenium oxides in which the alkyl may be cycloalkyl. In the case of these compounds, however, there is the disadvantage that high concentrations are required for use in protecting wood and their action is only slight against fungi that discolour wood and against bacteria that colonise wood.

For these reasons, there have been proposed (DE-OS 2 336 290, DE-OS 2 341 882) mixtures of aluminium salts of N'-hydroxy-N-alkyldiazenium oxides in which the alkyl may be cycloalkyl with other special biocides to increase the activity or broaden the range of action.

Surprisingly, we have now found that mixtures of trialkyltin compounds with alkali metal salts of N'-hydroxy-N-cyclohexyldiazenium oxide have a synergistic action, especially against gram-negative bacteria and fungi which belong to the class of the Ascomycetes and Fungi imperfecti and which are generally difficult to combat. An increase in action has also been found against gram-positive bacteria and against fungi that destroy wood.

10           The agents according to the invention can be used especially in the form of aqueous formulations, and are suitable, more especially, for the protection of wood, for example fresh-cut wood which is readily infested by bacteria and fungi such as those of the type Aspergillus and of Trichoderma. The agents can likewise be used to  
15           protect wood for building, the synergistic action of the active ingredients being effective against fungi that destroy wood and also against infestation by bacteria. Bacteria do not decompose wood, but can, however, aid an  
20           attack by fungi.

For use in aqueous formulations, the agents according to the invention can be prepared in the form of stable aqueous concentrates which contain emulsifiers suitable for the purpose, preferably non-ionic emulsifiers such, for example, as alkylarylpolyglycol ethers.  
25           The active ingredient mixture in such concentrates is present in a concentration of from 10 to 25 % by weight.

The concentrates can be diluted, without difficulty, to provide stable solutions for use.

Furthermore, the agents according to the invention are suitable for the biocidal treatment of aqueous paint systems, for example dispersions, as preservative and protection against infestation of the paint by bacteria and fungi, especially also against infestation of aqueous wood-paint systems, for example alkyd resin dispersions, by blue fungi.

10       The aqueous formulations can be used also for the biocidal treatment of different materials such as paper, cardboard, plastics materials, textiles, adhesives, building materials and leather.

15       A further area of use in the treatment of quantities of water against undesired microorganisms, for example circulating cooling water, manufacturing water in the case of paper production or drilling and cutting oils.

20       According to the field of use in each case, the concentrations of active ingredient may suitably be within the range of from 0.1 to 5 % by weight for protecting wood, from 0.05 to 3 % by weight for the treatment of paint systems, paper, textiles and building materials and from 0.0001 to 0.2 % by weight  
25       in the case of cooling and manufacturing water, and drilling and cutting oils.

The invention further provides a method of

combating bacteria or fungi which comprises treating a material or area infested with or liable to infestation by bacteria or fungi with an agent or aqueous formulation in accordance with the invention.

5       As the trialkyltin compound there may be used, more especially, a tri-n-butyltin compound, for example, tri-n-butyltin oxide, tri-n-butyltin linoleate, tri-n-butyltin naphthenate or tri-n-butyltin abietate. There also come into consideration the tripropyltin compounds.

10       The alkyl radicals may be the same or different provided the total number of carbon atoms is from 9 to 12.

          The alkali metal salt of N'-hydroxy-N-cyclohexyldiazenium oxide is preferably the potassium salt, but there may also be mentioned the sodium and lithium salts.

15       The following Examples illustrate the invention, the parts and percentages being by weight unless otherwise stated.

Example 1Formulation containing 10 % of active ingredient

- 4 parts by weight of tri-n-butyltin oxide  
20 parts by weight of a 30 % aqueous solution  
5 of the potassium salt of  
N'-hydroxy-N-cyclohexyl-  
diazonium oxide  
20 parts by weight of non-ionic emulsifier  
(Marlowet ISM)  
10 56 parts by weight of water

The components are homogenised by stirring and a clear to very slightly turbid mixture is obtained which, when diluted with tapwater to an approximate ratio of 1 : 50, yields stable, clear to slightly opalescent  
15 preparations. The non-ionic emulsifier (Marlowet ISM) is an alkylaryl polyglycol ether supplied by BASF. Marlowet ISM is a Registered Trade Mark.

Example 2Formulation containing 10 % of active ingredient

- 20 5.7 parts by weight of tri-n-butyltin linoleate  
14.3 parts by weight of a 30 % aqueous solution of  
the potassium salt of N'-  
hydroxy-N-cyclohexyl-  
diazonium oxide  
25 21.5 parts by weight of non-ionic emulsifier  
(Marlowet ISM)  
58.5 parts by weight of water

The components are homogenised by stirring and a clear to very slightly turbid mixture is obtained which, when diluted with tapwater to an approximate ratio of 1 : 50, yields stable, clear to slightly opalescent preparations.

### Example 3

#### Formulation containing 24 % of active ingredient

12 parts by weight of tri-n-butyltin naphthenate  
40 parts by weight of a 30 % aqueous solution of  
the potassium salt of N'-  
hydroxy-N-cyclohexyl-  
diazonium oxide  
48 parts by weight of non-ionic emulsifier  
(Marlowet ISM)

The components are homogenised by stirring and a clear to very slightly turbid mixture is obtained which, when diluted with tapwater to an approximate ratio of 1 : 100, yields stable, clear to slightly opalescent preparations.



Example 4Formulation containing 15 % of active ingredient

- 6 parts by weight of tri-n-butyltin abietate
- 30 parts by weight of a 30 % aqueous solution of
- 5 the potassium salt of N'-  
hydroxy-N-cyclohexyl-  
diazonium oxide
- 24 parts by weight of non-ionic emulsifier  
(Marlowet ISM)
- 10 40 parts by weight of water

The components are homogenised by stirring and a  
clear to very slightly turbid mixture is obtained  
which, when diluted with tapwater to an approximate  
ratio of 1 : 75 yields stable, clear to slightly  
15 opalescent preparations.

Table 1

For a comparison of action, circular paper filters (diameter 5.5 cm) were soaked with the aqueous solutions given in detail below, dried in air, then placed in

- 5 Petri dishes on plate-count agar which had been inoculated with suspensions of bacteria, and incubated for 2 days at +37°C. The size of the inhibition zones around the filters was then determined:

10	Active ingredient in solution	% by weight of active ingredient	Inhibition zones in mm		
			<u>Bacillus subtilis</u>	<u>Bacillus mesentericus</u>	<u>Proteus vulgaris</u>
15	Tri-n-butyltin oxide	1	12 - 15	12 - 15	5 - 7
		0.5	10 - 12	12 - 15	3 - 5
		0.2	10 - 12	10 - 12	0 - 1
	Tri-n-butyltin linoleate	1	6 - 7	7 - 8	2 - 3
		0.5	4 - 6	5 - 6	1 - 2
		0.2	2 - 3	3 - 4	0 - 1
20	K salt of N'-hydroxy-N-cyclohexyl-diazenium oxide	1	0 - 1	2 - 4	0
		0.5	0	0 - 1	0
		0.2	0	0 - 1	0
25	Example 1	1	>15	>15	12 - 15
		0.5	>15	>15	8 - 10
		0.2	10 - 12	>15	6 - 8
	Example 2	1	12 - 15	12 - 15	12 - 15
		0.5	10 - 12	10 - 12	12 - 15
		0.2	9 - 10	10 - 12	8 - 10

Table 2

In accordance with the method of Table 1, soaked round paper filters were placed on biomalt agar which had been sprayed with suspensions of spores of test fungi, and incubated for 3 weeks at +30°C. The inhibition zones around the samples were then determined:

Active ingredient in solution	% by weight of active ingredient	Inhibition zones in mm			
		Tricho- derma viride	Clado- sporium herbarum	Asper- gillus versicolor	Pullularia pullulans
Tri-n-butyltin oxide	1.0	4 - 6	6 - 8	6 - 8	2 - 3
	0.5	3 - 5	2 - 4	3 - 4	1 - 2
	0.2	2 - 3	0 - 1	1 - 2	0 - 1
Tri-n-butyltin naphthenate	1.0	2 - 3	2 - 3	3 - 4	1 - 2
	0.5	1 - 2	1 - 2	1 - 2	0 - 1
	0.2	0 - 1	0	0	0
Tri-n-butyltin abietate	1.0	2 - 3	1 - 2	2 - 3	1 - 2
	0.5	1 - 2	0 - 1	0 - 1	0 - 1
	0.2	0 - 1	0	0	0
K salt of N'- hydroxy-N-cyclo- hexyldiazonium oxide	1.0	0 *	5 - 7	2 - 4	6 - 8
	0.5	0 *	0	0 *	0
	0.2	0 *	0	0 *	0
Example 1	1	8 - 10	12 - 15	>15	12 - 15
	0.5	5 - 7	10 - 12	12 - 15	10 - 12
	0.2	2 - 3	8 - 10	10 - 12	10 - 12

Table 2 (continued)

Active ingredient in solution	% by weight of active ingredient	Inhibition zones in mm			
		<u>Tricho- derma viride</u>	<u>Clado- sporium herbarum</u>	<u>Asper- gillus versicolor</u>	<u>Pullularia pullulans</u>
Example 3	1	5	10 - 12	12 - 15	10 - 12
	0.5	3	8 - 10	10 - 12	10 - 12
	0.2	1	6 - 8	8 - 10	8 - 10
Example 4	1	4	10 - 12	12 - 15	10 - 12
	0.5	3	6 - 7	9 - 10	8 - 10
	0.2	2	4 - 5	6 - 8	6 - 8

\*) = strong growth of sample

Table 3

In accordance with the method of Table 2, the inhibition zones around the samples were determined:

Active ingredient in solution	% by weight of active ingredient	Inhibition zones in mm		
		<u>Chaetomium globosum</u>	<u>Poria monticula</u>	<u>Lenzitis trabea</u>
5 Tri-n-butyltin oxide	0.5	8 - 10	7 - 9	10 - 12
	0.2	6 - 8	5 - 7	6 - 8
10 Tri-n-butyltin linoleate	0.5	3 - 4	3 - 4	5 - 7
	0.2	1 - 2	1 - 2	2 - 3
Tri-n-butyltin naphthenate	0.5	2 - 3	2 - 3	4 - 5
	0.2	0 - 1	1 - 2	2 - 3
15 K salt of N'-hydroxy-N-cyclohexyl diazenium oxide	0.5	2 - 3	4 - 6	4 - 5
	0.2	0	0	0
Example 1	0.5	12 - 15	8 - 10	12 - 15
	0.2	8 - 10	6 - 8	8 - 10
20 Example 2	0.2	3 - 4	3 - 4	4 - 6
Example 3	0.5	5 - 7	4 - 5	6 - 8
	0.2	2 - 3	3 - 4	4 - 5

For a comparison of action, small blocks of pine sapwood measuring 5 x 2.5 x 1.5 cm were soaked in the following solutions of active ingredient:

- 25 A 2 % tri-n-butyltin naphthenate
- B 2 % potassium salt of N'-hydroxy-N-cyclohexyl-diazenium oxide
- C 2 % the mixture of active ingredients specified
- 30 in Example 3
- D without active ingredient.

After drying and sterilisation, one small block in each case without active ingredient and with active ingredient was inserted into a Kalle dish having biomalt agar which had been sprayed with a suspension of spores of the test fungi, and incubated for 10 weeks at +30°C. The growth of the fungi mycelium at and on the samples was then assessed visually:

Inhibitory action of soaked small wood blocks against test fungi in the Kalle dish test.

10	Soaking solution	Take-up of active ingredient % by weight	Test fungi		Pullularia Pullulans Growth of the sample*	IZ*
			Trichoderma viride			
			Growth of the sample*	IZ*		
15	A	0.031	-	1 - 2		
	D	-	+++	0		
	A	0.033			-	0 - 1
	D	-			+++	-
20	B	0.034	++	0		
	D	-	+++	0		
	B	0.030			-	1 - 2
	D	-			+++	0
	C	0.029	-	4 - 5		
	D	-	+++	0		
25	C	0.033			-	3 - 4
	D	-			+++	0

\*) Growth of the sample

- = no growth  
 + = slight growth  
 ++ = moderate growth  
 +++ = strong growth  
 IZ = Inhibition zone around the sample in mm.

26. A method of combating bacteria or fungi which comprises treating an aqueous paint system with an aqueous formulation as claimed in claim 7, 8 or 9.

27. A method of combating bacteria or fungi which comprises treating a material infected with gram-negative bacteria and fungi which belong to the class of the Ascomycetes and Fungi imperfecti, with an aqueous formulation as claimed in claim 7, 8 or 9.

**SUBSTITUTE**

***REPLACEMENT***

**SECTION is not Present**

***Cette Section est Absente***



THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A bactericidal or fungicidal aqueous concentrate containing a) a trialkyltin compound having in the alkyl groups bonded to the tin atom a total number of from 9 to 12 carbon atoms or a triphenyltin compound excluding triorgano-tin halides and b) an alkali metal salt of N'-hydroxy-N-cyclohexyl-diazenium oxide, the components (a) and (b) being present in a ratio of from 5:1 to 1:5, by weight respectively.

2. A concentrate as claimed in claim 1, wherein the components (a) and (b) are present in a ratio of from 3:1 to 1:3 by weight, respectively.

3. A concentrate as claimed in claim 1, 2 ~~or 3~~, wherein component (a) is a tri-n-butyltin compound.

4. A concentrate as claimed in claim 1, 2 ~~or 3~~, wherein component (a) is tri-n-butyltin oxide, tri-n-butyltin linoleate or tri-n-butyltin naphthenate.

5. A concentrate as claimed in claim 1, 2 ~~or 3~~, wherein component (b) is the potassium salt of N'-hydroxy-N-cyclohexyldiazenium oxide.

6. A concentrate as claimed in claim 1, which contains from 10 to 25% by weight of the active ingredient mixture (a) and (b).

7. An aqueous formulation which comprises a bactericidal or fungicidal formulation as claimed in claim 1 diluted with water and containing an emulsifying agent.

8. An aqueous formulation as claimed in claim 7, wherein the emulsifying agent is a non-ionic emulsifying agent.

9. An aqueous formulation as claimed in claim 8, wherein the emulsifying agent is an alkylaryl polyglycol ether.

10. An aqueous formulation as claimed in claim 7, which contains from 0.1 to 5% by weight of the active ingredient mixture (a) and (b).

11. An aqueous formulation as claimed in claim 7, which contains from 0.05 to 3% by weight of the active ingredient mixture (a) and (b).

12. An aqueous formulation as claimed in claim 7, which contains from 0.1 to 3% by weight of the active ingredient mixture (a) and (b).

13. An aqueous formulation as claimed in claim 7, which contains from 0.0001 to 0.2% by weight of the active ingredient mixture (a) and (b).

14. An aqueous formulation as claimed in claim 7, wherein the components (a) and (b) are present in a ratio of from 3:1 to 1:3 by weight, respectively.

15. An aqueous formulation as claimed in claim 7, wherein component (a) is a tri-n-butyltin compound.

16. An aqueous formulation as claimed in claim 7, wherein component (a) is tri-n-butyltin oxide, tri-n-butyltin linoleate or tri-n-butyltin naphthenate.

17. An aqueous formulation as claimed in claim 7, wherein component (b) is the potassium salt of N'-hydroxy-N-cyclohexyldiazenium oxide.

18. A method of combating bacteria or fungi which comprises treating a material or area infested with or liable

to infestation by bacteria or fungi with a formulation as claimed in claim 7, 8 or 9.

19. A method of combating bacterial or fungi which comprises treating a material or area infested with or liable to infestation by bacteria or fungi with an aqueous formulation as claimed in claim 10, 11 or 12.

20. A method of combating bacteria or fungi which comprises treating a material or area infested with or liable to infestation by bacteria or fungi with an agent as claimed in claim 13, 14 or 15.

21. A method of combating bacteria or fungi which comprises treating a material or area infested with or liable to infestation by bacteria or fungi with an agent as claimed in claim 16 or 17.

22. A method of combating bacteria or fungi which comprises treating wood with an aqueous formulation as claimed in claim 7, 8 or 9.

23. A method of combating bacteria or fungi which comprises treating wood with an aqueous formulation as claimed in claim 7, 8 or 9, containing from 0.1 to 3% by weight of the active ingredient mixture (a) and (b).

24. A method of combating bacteria or fungi which comprises treating paper, cardboard, plastic material, textile material, an adhesive, a building material or leather, with an aqueous formulation as claimed in claim 7, 8 or 9.

25. A method of combating bacteria or fungi which comprises treating circulating cooling water, water used in paper production or a drilling and cutting oil, with an aqueous formulation as claimed in claim 7, 8 or 9.

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ABSTRACT OF THE DISCLOSURE

The invention relates to an agent that can be diluted with water, has a bactericidal and fungicidal and contains an active ingredient mixture comprising: a) a trialkyltin compound having in the alkyl groups bonded to the tin of a total number of from 9 to 12 carbon atoms or a triphenyltin compound excluding triorgano-tin halides, and b) an alkali metal salt of N'-hydroxy-N-cyclohexyldiazenium oxide.

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